Natural Gas and Oil Technology Partnership Proposal
Upstream Environmental Program
Use of Ionic Liquids in Produced Water Clean Up

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Statement of Problem: Discharge of produced water in the Gulf of Mexico is regulated by NPDES permits, which specify that total oil and grease in the water be below a daily maximum of 42 ppm. Analysis of produced water for total petroleum hydrocarbons by EPA methods 413.1 or 1664 does not discriminate between recoverable oil and grease and water-soluble organic (WSO) compounds, mainly organic acids. Remediation of the close-to-trillion barrels per annum of produced water is currently done by acid springing, often with unpredictable results. Both of these problems arise from the chemistry of the oil and its ability to buffer against pH changes. The problem is particularly severe for new wells, where the properties of the oil may change during springing, and the amounts and types of the water-soluble organic compounds are not well known. Hence, the goal of this project will be to introduce a new approach to produced water sampling, through solvent extraction using ionic liquids. If successful, this method could be extended to remediation of produced water, as a step following acid springing and filtration.

Comparison of New to Existing Technologies

The core of the problem with produced water is separation of oil and grease from the aqueous phase, separation of the oil and grease from water-soluble organic compounds, and demonstration of successful separation to the regulating agency. Improvements in separation can be achieved by changing physical constraints, such as temperature and pressure, or by using a new solvent – the approach proposed here. Ionic liquids are salts that are liquid at room temperature, consisting of ring-stabilized cations and smaller fluorinated anions. Ionic liquids have many advantages as solvents.

- Their structures can be tailored to optimize a specific separation.
- They have negligible vapor pressures, which reduces environmental impact,
- They are noncombustible.
- They are effective at relatively high solute concentrations (up to 1000 ppm).
- Very high distribution coefficients (concentration in ionic liquid divided by that in water) are possible.

The potential for use of ionic liquids is only starting to be realized for both inorganic and organic separations. At ORNL, ionic liquids have been used to successfully separate acetone from air, and to partition permanent gases such as CO_2 and N_2. Separations such as these, based on Henry's law coefficients, should also be effective in the detection and removal of hydrocarbons from produced water brines.

Application and Benefits of the New Technology to Industry:

Ionic liquids may offer enhancements to produced water remediation methods currently in use. The first step in this project will be to evaluate whether an ionic liquid supported on a quartz crystal microbalance (QCM) can be used as a chemical sensor for hydrocarbons entrained in the aqueous phase. This technology, used elsewhere for chemically sensitive detection, can be employed by the petroleum industry to sample directly for water-soluble organic components in produced water once the residual oil and grease have been removed. This sensing technology has been shown to be sensitive to nanogram levels, reproducible, robust and quick. Hence, it would allow an on-line test of the efficiency of acid springing, before rigorous testing with EPA methods. Production line problems, such as fluctuating pH, could then be handled swiftly and effectively. Another application may be to use ionic liquids to target specific harmful compounds through liquid-liquid extraction from produced water.

Tasks and Contributions of the Research Team:

In this project, ORNL and industry partners are addressing questions regarding efficacy, regeneration, and selectivity of ionic liquid-based removal of polar organic compounds from produced water. For produced-water sensors and remediation, the ionic liquid must be immiscible with the aqueous phase. Some hydrophobic ionic liquids are available commercially and others are synthesized in-house. The ionic liquids are being tested in two ways:

(1) in the liquid-liquid extraction of produced water contaminants. Extraction and regeneration are being studied as a function of physical and chemical variables such as pH, temperature, salinity and the presence of other organics. A variety of ionic liquids have been tested in FY2003 to optimize the chemistry of the anion and cation, and this will continue as new formulations become available. The produced water is analyzed by High Performance Liquid Chromatography (HPLC) or Gas Chromatography (GC) to determine water-soluble organic content. In addition, the ionic liquid itself is analyzed by UV or nuclear magnetic resonance (NMR) spectroscopy for organic contamination and degradation. Losses of the ionic liquid through dissolution into the aqueous phase or through decomposition are monitored. Data from these tests yield separation factors, which will be used in engineering calculations. A side benefit; however, will be that the chemical classification of the WSO component is also of use in produced water modeling, an ongoing project at ORNL.

(2) as part of a sensor. The sensor will consist of a quartz crystal microbalance (QCM) coated with ionic liquid. Initial tests involve detection of organic in the gas phase, carried to the sensor in a flow of nitrogen that bubbles through a solution of brine loaded with water-soluble organics. The project will also test a QCM device that operates in the liquid phase. Performance of the sensors will be measured in terms of sensitivity, selectivity, linearity of response, losses and ability to regenerate the ionic liquid.

Tasks:
1. Selection/synthesis of ionic liquids tailored to the separation of interest and minimization of ionic liquid loss during separation and recovery.
2. Preparation of samples, including simulated brines. Testing of actual produced water samples from oil and gas producers.
3. Quantification of separation factors by analysis of the produced water and the ionic liquid phase using NMR and UV spectroscopy, HPLC and GC.
4. Analysis of performance (e.g., as a function of pH). Identification of problems (e.g., chemical interferences).
5. Development of a QCM sensor based on the most successful ionic-liquid separation from proof-of-principle experiments.
6. Evaluation of the technology (i.e., distribution coefficients, losses, cost of ionic liquid and stripping/regeneration) for application to targeted produced water remediation.

Deliverables:

FY2003
- Synthesis and/or acquisition of ionic liquids suitable for WSO removal from produced water.
- Documentation of successful ionic liquid separations based on simulated and actual produced water samples.

FY2004
- Documentation of the dependence of ionic-liquid based separations on temperature, pressure, and pH, and potential barriers before use in the field.
- Demonstration of a WSO sensor using an ionic-liquid coated QCM.

FY2005
- Development of ionic-liquid based sensor for field use.
- Evaluation of separation technology to targeted produced water remediation.

Why DOE funding is required:

The produced water waste stream is of concern to all oil producers, large companies as well as the smaller independent producer. Off shore and on-shore facilities alike will benefit from the ability to remediate produced water using methods that are both efficient and cost-effective. The government has a role in assisting all producers to comply with environmental regulations, and to ensure a diverse and secure energy supply. Research into a new approach, such as applying ionic liquids to solving problems with produced water, may not otherwise be pursued in industrial laboratories because it is based on recent technological developments.

Critical Decision Points

September 2003: Ionic liquids involving the Tf_2N anion appear to perform best in hydrocarbon removal.

May 2004: Evaluate success of ionic liquid extraction of aqueous hydrocarbons. If successful, then continue development of QCM sensor. Continue assessment of different formulations of ionic liquids.

September 2004: Evaluate success of QCM sensor under a variety of conditions. Continue with development of a field instrument, or perform an engineering feasibility study on the scale up the separation procedure to targeted produced water remediation.

Accomplishments in FY2003

The extraction of simulated water soluble organics has been demonstrated with ionic liquids under physical and chemical conditions similar to that encountered in Gulf of Mexico produced water. A quartz crystal microbalance apparatus was commissioned for detection of organic molecules in produced water.

Considerable progress was achieved towards the FY2003 deliverables.

- Synthesis and/or acquisition of ionic liquids suitable for WSO removal from produced water.

Distribution coefficients of organic compounds between water and three room temperature hydrophobic ionic liquids were measured. The polar organics studied to date were typical of produced water contaminants: organic acids (hexanoic and acetic acid), alcohols (1-nonanol and butane diol), and aromatics (toluene). The physical properties of ionic liquids, such as hydrophobicity, can be tailored for a particular application by changing the cation or anion. Hence, in the current series of tests, three different ionic liquids were selected for investigation, butylmethylimidazolium bistrifluoromethylsulfonyl amide - bmim Tf_2N, octylmethylimidazolium Tf_2N – omim Tf_2N, and bmim PF_6. Ionic liquids and aqueous solutions of the organics were contacted under static conditions. Concentrations of organics in the aqueous phase and similarly treated controls were measured by gas chromatography and high performance liquid chromatography, and the distribution coefficients were obtained through a mass balance. Sensitivity of solubility to salinity, temperature, concentration, and pH were determined. Partitioning into the ionic liquid varied considerably. Some distribution coefficients (concentration in the ionic liquid divided by concentration in the aqueous phase) were as high as several hundred for toluene and for 1-nonanol. The uptake of butane diol and the fatty acids; however, was marginal in the ionic liquids tested. The highest distribution coefficients were observed with omim Tf_2N. The distribution coefficients for hexanoic acid and 1-nonanol appeared to be pH sensitive; higher for the hexanoic acid at low pH suggesting that the protonated form was preferentially removed from aqueous solution, and higher for 1-nanonol at high pH. This pH sensitivity may assist in regenerating the ionic liquid. The distribution coefficients for toluene, 1-nonanol, and hexanoic acid were independent of ionic liquid-to-water ratio over the range from 0.02 to 1.0. Bmim Tf_2N showed a large capacity for organics, up to 100 $g{\cdot}L^{-1}$; and regeneration trials were also successful. Many of the organics could be removed from the ionic liquid by rinsing or volatilization. These experiments have shown that ionic liquids do have an affinity for produced water contaminants, and so there is potential for their use in sensing and removal of water soluble organics. The quartz crystal microbalance sensor is now being commissioned for the detection of organics in produced water.

In addition to the liquid-liquid extraction experiments, ORNL had the opportunity to pass the ionic liquid-brine system through a centrifugal contactor, to determine if this separation technology could be used to extract organics from produced water. The experiments successfully demonstrated the separation of bmim Tf_2N – 1 M NaCl and Terrasail™ – 1 M NaCl. Both bmim Tf2N and Terrasail™ are hydrophobic but have different densities. Other physical properties of the ionic liquids were measured, including viscosity, thermal behavior (stability up to 300°C), and surface tension at the brine-ionic liquid interface.

- Documentation of successful ionic liquid separations based on simulated and actual produced water samples.

Two posters were presented at the Separations Science and Technology Conference in Gatlinburg, TN, October 27. One, titled “Room Temperature Ionic Liquids Separating Organics from Produced Water” described the ionic liquid extraction of organics from aqueous solution. The other, “Separation of Ionic Liquid Dispersions in Centrifugal Solvent Extraction Contactors” was on the separation of ionic liquid and brine in the centrifugal contactor. A full paper has been written for each of these topics and both of these papers have been sent for external review before publication in the Separation Science and Technology Journal.

J. McFarlane and W.B. Ridenour, “Room Temperature Ionic Liquids for Separating Organics from Produced Water”, submitted to Separations Science and Technology.

Joseph F. Birdwell, Jr., Huimin Luo, Joanna McFarlane, Rodney D. Hunt, and David W. DePaoli, “Separation of Ionic Liquid Dispersions in Centrifugal Solvent Extraction Contactors”, submitted to Separations Science and Technology.